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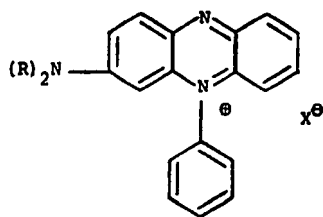
(58) Field of search

C7B

(54) **Electrodeposition of copper**

(57) An aqueous acidic electrolyte for electrodepositing an exceptionally bright, levelled and ductile copper deposit comprises a synergistic combination of:

- (a) a substituted phthalocyanine compound, and
(b) an apo safranine compound represented by the formula:



wherein:

R independently represents $-CH_3$, $-C_2H_5$ and $-C_3H_7$; and

X represents a chloride, bromide, iodide, fluoride, sulphate, bisulphate or nitrate ion.

The electrolyte preferably also includes supplemental brightening agents such as organic polysulphides, sulphides and/or polyether compounds.

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SPECIFICATION

Electrodeposition of copper

- 5 The present invention broadly relates to an aqueous electrolyte composition and process for electrodepositing copper on a conductive substrate and, more particularly, to an improved aqueous acidic copper plating bath containing a novel combination of brightening agents to provide a copper plate which is ductile, level and bright particularly in the low current density recess areas. 5
- 10 A variety of aqueous electrolyte compositions and processes have heretofore been used or proposed for use for electrodepositing bright, level ductile copper deposits. Typical of such prior art compositions and processes are those described in U.S. Patent Nos. 2,707,166; 2,707,167; 2,738,318; 2,882,209; 3,267,010; 3,328,273; 3,770,598; 4,110,176 and 4,272,335. In accordance with the teachings of United States Patent No. 4,272,335 an 10
- 15 improved aqueous acidic copper electrolyte is provided which contains a substituted phthalocyanine compound as a brightening agent which in accordance with the preferred disclosure further incorporates supplemental secondary brightening agents such as polysulphides, sulphides and/or polyether compounds. While the aqueous acidic electrolyte as described in the aforementioned United States patent provides for improvements in the brightness, levelling and 15
- 20 ductility of copper platings, under certain operating parameters and composition variations, less than optimum brightness of the copper plate has been obtained in the low current density recess areas of articles being plated. 20
- On the other hand, when an apo safranine brightening compound has been employed alone or in further combination with supplemental brightening agents such as polysulphides, organic 25
- 25 sulphides and/or polyether compounds, unsatisfactory brightness and levelling of the deposit has been obtained under certain conditions in low current density areas. An increase in the concentration of the apo safranine brightening compound to overcome the low current density problem resulted in the formation of dark striations in the low current density areas producing an unacceptable deposit. 25
- 30 There, accordingly, has been a need for a still further improvement in aqueous acidic copper electrolytes to provide exceptional brightness of copper deposits in the low current density recess areas of articles being plated which can be consistently attained over a broad range of composition and processing conditions. The aqueous acidic electrolyte of the present invention incorporates a selected combination of brightening agents providing for a synergistic brightening 30
- 35 effect, particularly in such low current density recess areas over a relatively broad range of concentrations and bath operating conditions. 35
- The benefits and advantages of the present invention are achieved by an electrolyte composition and process for electro-depositing copper from an aqueous acidic plating bath containing a brightening amount of a combination of a bath soluble compound including a 40
- 40 substituted phthalocyanine radical and an apo safranine compound present in controlled amounts. More particularly, the aqueous acidic electrolyte is preferably of the copper sulphate or fluoroborate type and incorporates copper in an amount sufficient to electrodeposit copper, and a brightening amount of the substituted phthalocyanine radical represented by the formula: 40
- 45 PcX_n 45
- wherein:
- Pc represents a phthalocyanine radical;
- X represents $-SO_2NR_2$, $-SO_3M$ or $-[CH_2SC(NR_2)_2]^+Y^-$;
- 50 R represents a hydrogen atom, an alkyl group containing 1 to 6 carbon atoms, an aryl group containing 6 carbon atoms, an aralkyl group containing 6 carbon atoms in the aryl portion and 1 to 6 carbon atoms in the alkyl portion, or a heterocyclic group containing 2 to 5 carbon atoms and at least 1 nitrogen, oxygen, sulphur or phosphorus atom, each of the alkyl, aryl, aralkyl and heterocyclic groups, as defined above, optionally being substituted with 1 to 5 amino, hydroxy, 55
- 55 sulphonic or phosphonic groups; 55
- n is an integer of from 1 to 6;
- Y represents halogen or alkyl sulphate containing 1 to 4 carbon atoms in the alkyl portion; and
- M represents a hydrogen, lithium, sodium, potassium or magnesium atom in further 60
- 60 combination with a compound represented by Formula A: 60

FORMULA A



wherein:

- 15 R independently represents $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ or $-\text{C}_3\text{H}_7$; and
 X represents a chloride, bromide, iodide, fluoride, sulphate, bisulphate or nitrate ion.

The phthalocyanine brightening agent may be metal-free or may contain a stable divalent or trivalent metal, such as cobalt, nickel, chromium, iron, or copper, of which copper constitutes the preferred metal. A mixture of phthalocyanine brightening agents containing different metal atoms may be provided. Phthalocyanine brightening agents suitable for use in the practice of the present invention generally will have a bath solubility of at least about 0.1 milligrams per litre (mg/l).

In accordance with a preferred practice of the present invention, the phthalocyanine and apo safranine brightening agents are supplemented by the addition of secondary brightening agents including aliphatic polysulphides, organic sulphides and/or polyether compounds to further enhance the brightness and physical properties of the copper deposit.

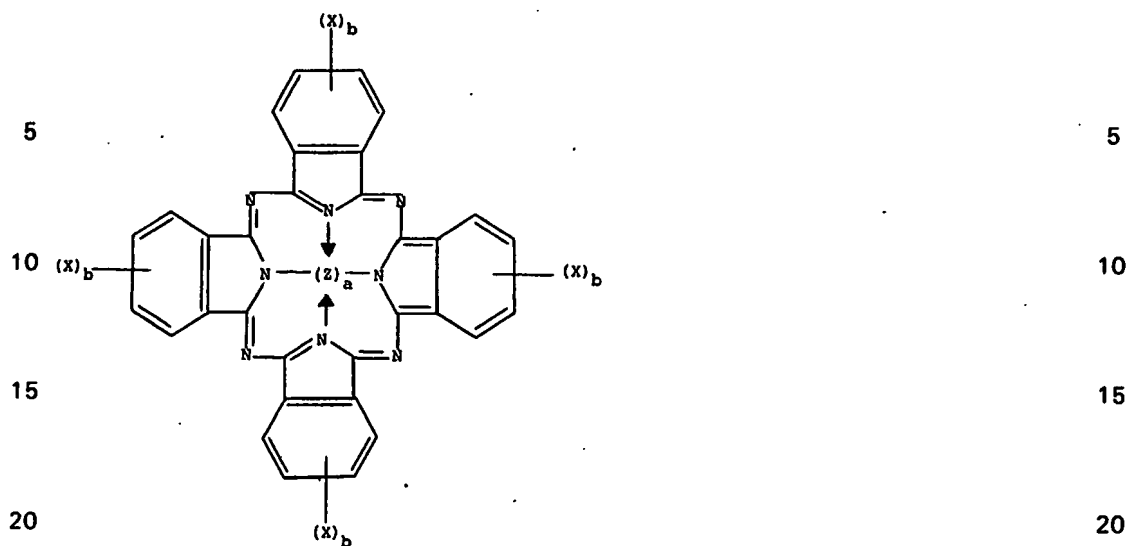
In accordance with the process aspects of the present invention, the aqueous acidic electroplating bath can be operated at temperatures ranging from about 15° up to about 50°C and at current densities ranging from about 0.5 to about 400 amperes per square foot (ASF) (0.055 to 44 amperes per square decimetre (ASD)).

Additional benefits and advantages of the present invention will become apparent upon a reading of the following description of the preferred embodiments taken in conjunction with the accompanying examples.

In accordance with the practice of the process of the present invention, an aqueous acidic electrolyte is provided which may be of the sulphate type typically containing about 180 to about 250 g/l of copper sulphate and about 30 to about 80 g/l of sulphuric acid. Alternatively, fluoroborate baths can be prepared typically containing from about 200 to about 600 g/l of copper fluoroborate and up to about 60 g/l of fluoboric acid. It is also contemplated that copper nitrate salts can be employed in approximately equivalent proportions for copper sulphate and the electrolyte can be acidified employing equivalent amounts of phosphoric acid, nitric acid or sulphuric acid. In accordance with the preferred practice of the present invention, sulphate-type copper baths are employed.

The aqueous electrolyte may further incorporate halide ions such as chloride and/or bromide ions in an amount up to about 0.5 g/l.

The exceptional brightening obtained in the low current density recess areas is achieved by employing a synergistic combination of the substituted phthalocyanine radical brightening agent and the apo safranine brightening agent in controlled concentrations and proportions, preferably in further combination with supplemental organic brightening agents. The substituted phthalocyanine radical which may be metal-free or which may contain a stable divalent or trivalent metal bound by coordination of the isoindole nitrogen atoms of the molecule, which metal is selected from the group consisting of cobalt, nickel, chromium, iron or copper, of which copper is the more typical and preferred metal. A mixture of different metal-containing phthalocyanine compounds may be used. Phthalocyanine compounds particularly suitable for use in the practice of the present process are those having a bath solubility of at least about 0.1 mg/l and corresponding to the structural formula:



wherein:

X is as has been heretofore defined;

Z represents a nickel, cobalt, chromium, iron or copper atom;

a is 0 or 1; and

b is independently 0, 1 or 2 provided however that the total number of X substituents is 1-6.

Substituted phthalocyanine compounds suitable for use in the practice of the present invention further include those as described in United States Patent No. 4,272,335 and teachings of which are incorporated herein by reference. A particularly preferred phthalocyanine compound comprises Alcian Blue.

The combined brightening agents corresponding to Formula A and the substituted phthalocyanine radical brightening agent may be employed at a bath concentration of from about 0.005 g/l up to about 1 g/l with concentrations of about 0.002 g/l to about 0.01 g/l being preferred. The substituted phthalocyanine radical brightening agent can form from about 35 up to about 80 percent by weight of the combined weight of the two brightening agents employed. A particularly satisfactory combination comprises employing Methic Turquoise as the substituted phthalocyanine brightening agent at a concentration of 3 mg/l in combination with an apo safranine brightening agent represented by Formula A in which R comprises ethyl also present at a concentration of 3 mg/l.

In addition to the substituted phthalocyanine and apo safranine brightening agents, it has been found advantageous in accordance with the practice of the present invention to incorporate at least one additional supplemental brightening agent of the types known in the art to further enhance the brightness, ductility and levelling of the electrodeposited copper. Included among such supplemental brightening agents are polyether compounds and organic sulphide and disulphide compounds.

The preferred organic polyether compounds are bath soluble and compatible polyethers containing at least 4 ether oxygen atoms and having an average molecular weight ranging from about 180 up to 1,000,000. Particularly satisfactory results are obtained with polypropylene and polyethylene glycols including mixtures of the foregoing of an average molecular weight of about 600 to about 6,000, and alkoxyated aromatic alcohols having a molecular weight ranging from about 300 to 2500. Exemplary of such preferred polyether brightening compounds which can satisfactorily be employed are polyethylene glycols of an average molecular weight of from about 400 to about 1,000,000; ethoxylated naphthols containing 5 to 45 mols ethylene oxide groups; propoxylated naphthols containing 5 to 15 mols of propylene oxide groups; ethoxylated nonyl phenol containing 5 to 30 mols ethylene oxide groups; propylene glycols of an average molecular weight of about 350 to about 1,000; block polymers of polyoxyethylene and polyoxypropylene glycols of an average molecular weight of about 350 to 250,000; ethoxylated phenols containing 5 to 100 mols of ethylene oxide groups; propoxylated phenols containing 5 to 15 mols of propylene oxide groups, and ethylene diamine block polymers having a molecular weight of about 1600 to about 30,000. Additional polyether compounds suitable for use in the practice of the present process are those disclosed in United

States Patent No. 4,272,335 the teachings of which are incorporated herein by reference.

The polyether brightening compounds are employed in a range of about 0.001 up to about 5 g/l with the lower concentrations generally being used with the higher molecular weight polyethers.

- 5 Organic sulphide brightening compounds which can be satisfactorily employed in the practice of the present process includes the various sulphonate organic sulphide compounds as described in United States Patent No. 3,267,010, and particularly Table I thereof, the teachings of which are incorporated herein by reference; organic sulphur compounds as disclosed in United States Patent No. 4,181,582, and particularly Table III thereof, the substance of which is incorporated herein by reference; and the organic polysulphide compounds as disclosed in United States Patent No. 3,328,273 and particularly Table I thereof, the substance of which is also incorporated herein by reference. The organic sulphide compounds containing sulphonic or phosphonic groups may also contain various substituent groups, such as methyl, chloro, bromo, methoxy, ethoxy, carboxy or hydroxy, on the molecules, especially on the aromatic and heterocyclic sulphide-sulphonic or phosphonic acids. Such compounds may be used as the free acids, the alkali metal salts, organic amine salts, or the like.

Other suitable organic divalent sulphur compounds which can be satisfactorily used include $\text{HO}_3\text{P}-(\text{CH}_2)_3-\text{S}-\text{S}-(\text{CH}_2)_3-\text{PO}_3\text{H}$, as well as mercaptans, thiocarbamates, thiolcarbamates, thioanthates, and thiocarbonates which contain at least one sulphonic or phosphonic group.

- 20 A particularly preferred group of organic divalent sulphur compounds as described in U.S. Patent No. 3,328,273 are the organic polysulphide compounds of the formula $\text{XR}_1-(\text{S})_n\text{R}_2\text{SO}_3\text{H}$ or $\text{XR}_1-(\text{S})_n\text{R}_2\text{PO}_3\text{H}$ wherein R_1 and R_2 are the same or different alkylene group containing from about 1 to 6 carbon atoms, X is hydrogen, SO_3H or PO_3H and n is a number from about 2 to 5. These organic divalent sulphur compounds are aliphatic polysulphides wherein at least two divalent sulphur atoms are vicinal and wherein the molecule has one or two terminal sulphonic or phosphonic acid groups. The alkylene portion of the molecule may be substituted with groups such as methyl, ethyl, chloro, bromo, ethoxy, hydroxy, and the like. These compounds may be added as the free acids or as the alkali metal or amine salts.

- The organic sulphide brightening compound or mixture of compounds may be present in the electrolyte within a range of about 0.0005 to about 1 g/l.

- In accordance with the process aspects of the present invention, an aqueous acidic copper electrolyte of the foregoing composition is employed in which an electrically conductive substrate is immersed and is cathodically charged for a period of time to deposit the desired thickness of copper thereon. During the electroplating operation, the bath is controlled at a temperature of from about 15° up to about 50°C and at cathode current densities ranging from as low as about 0.5 to as high as about 400 ASF, (44 ASD), preferably from about 10 to about 100 ASF (1.1 to 11 ASD). Particularly satisfactory results are obtained at bath temperatures of about 20° to about 36°C at current densities of about 10 to about 50 ASF (1.1 to 5.5 ASD).

- In order to further illustrate the present invention, the following typical examples are provided. It will be appreciated that the examples are provided for illustrative purposes and are not intended to be limiting of the scope of the present invention as herein described and as set forth in the subjoined claimed.

EXAMPLE 1A

- 45 An aqueous acidic copper electrolyte is prepared containing about 165 g/l copper sulphate pentahydrate, about 42 g/l sulphuric acid and about 0.04 g/l chloride ions. To the foregoing aqueous solution, 3 mg/l of Methic Turquoise comprising the phthalocyanine brightening agent is added along with 3 mg/l of diethyl apo safranine. As supplemental brightening agents, the bath further contains 50 mg/l of polypropylene glycol of an average molecular weight of 700 and 20 mg/l of Bis (3-sulphopropyl disulphide disodium salt).

Operation of the bath at a current density of from about 0.5 to about 100 ASF (0.055 to 11 ASD) at a temperature of from about 70° to about 80°F (21° to 27°C) produced highly levelled, fine-grained copper deposits with no physical defects.

55 EXAMPLE 1B

An electrolyte similar to that of Example 1A is prepared except that it contains about 225 g/l copper sulphate pentahydrate, about 75 g/l sulphuric acid and about 0.1 g/l chloride ions. Operation of the bath in the same way as that of Example 1A gave similar results.

60 EXAMPLE 2A

- An aqueous acidic copper electrolyte is prepared containing about 165 g/l copper sulphate pentahydrate, about 42 g/l sulphuric acid and about 0.04 to 0.1 g/l chloride ions. To the foregoing aqueous solution, 3 mg/l of Methic Turquoise comprising the phthalocyanine brightening agent is added along with 60 mg/l of a block polymer of ethylene propylene oxide (mol wt. 3000), 20 mg/l of Bis (3-sulphopropyl disulphide disodium salt) and 1.5 mg/l of the

reaction product of polyethylene imine (mol wt. 600) with benzyl chloride as supplemental brightening agents.

- The operation of the bath at a temperature of from about 70° to about 80°F (21° to 28°C) and at current densities of about 20 to about 80 ASF (2.2 to 8.8 ASD) produces bright, levelled copper deposits. The further addition of 3 mg/l of diethyl apo safranine to the electrolyte results in a dramatic improvement in the levelling characteristics of the deposit and also substantially improves the brightness in the low current density areas of test panels employing the same plating parameters.

10 EXAMPLE 2B

An electrolyte similar to that of Example 2A is prepared except that it contains about 225 g/l copper sulphate pentahydrate, about 75 g/l sulphuric acid and about 0.1 g/l chloride ions.

Operation of the bath in the same way as Example 2A gave similar results.

15 EXAMPLE 3A

- An aqueous acidic copper electrolyte is prepared containing about 165 g/l copper sulphate pentahydrate, about 42 g/l sulphuric acid and about 0.04 g/l chloride ions. To the foregoing aqueous solution, 2 mg/l of diethyl apo safranine is added in further combination with supplemental brightening agents comprising 20 mg/l Bis (3-sulphopropyl disulphide disodium salt), 200 mg/l polyethylene oxide (mol wt. 6000) and 1.5 mg/l of a reaction product of polyethyleneimine (mol wt. 600) reacted with benzyl chloride.

- The foregoing electrolyte produces a bright, levelled copper deposit when plated on a J-shaped test panel at an average current density of about 50 ASF (5.5 ASD) for a period of 15 minutes but the deposit is striated in the low current density area. The addition of 3 mg/l of Methic Turquoise comprising the substituted phthalocyanine radical brightening agent to the electrolyte results in the elimination of the striations in the low current density area of the J-type test panel plated under the same conditions without any loss of brightness and levelling of the copper deposit.

30 EXAMPLE 3B

An electrolyte similar to that of Example 3A is prepared except that it contains about 225 g/l copper sulphate pentahydrate, about 75 g/l sulphuric acid and about 0.1 g/l chloride ions.

Operation of the bath in the same way as that of Example 3A gave similar results.

- While it will be apparent that the preferred embodiments of the invention disclosed are well calculated to fulfill the objects above stated, it will be appreciated that the invention is susceptible to modification, variation and change without departing from the proper scope or fair meaning of the subjoined claims.

CLAIMS

1. An aqueous acidic electrolyte containing copper in an amount sufficient to electrodeposit copper on a substrate and a brightening amount sufficient to produce a bright, levelled and ductile copper electrodeposit of a combination of brightening agents comprising:

(a) a substituted phthalocyanine compound represented by the formula:



wherein:

Pc represents a phthalocyanine radical;

X represents $-\text{SO}_2\text{NR}_2$, $-\text{SO}_3\text{M}$, or $-\text{[CH}_2\text{SC(NR}_2)_2\text{]}^{\oplus}\text{Y}^{\ominus}$

- R represents a hydrogen atom, an alkyl group containing 1 to 6 carbon atoms, an aryl group containing 6 carbon atoms, an aralkyl group containing 6 carbon atoms in the aryl portion and 1 to 6 carbon atoms in the alkyl portion, or a heterocyclic group containing 2 to 5 carbon atoms and at least 1 nitrogen, oxygen, sulphur or phosphorus atom, each of the alkyl, aryl, aralkyl and heterocyclic groups, as defined above, being optionally substituted with 1 to 5 amino, hydroxy, sulphonc or phosphonic groups;

n is an integer of from 1 to 6;

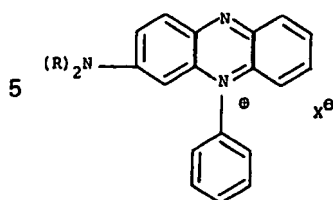
Y represents halogen or alkyl sulphate containing 1 to 4 carbon atoms in the alkyl portion;

and

M represents a hydrogen, lithium, sodium, potassium or magnesium atom;

- (b) an apo safranine compound represented by the formula:

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wherein:

R independently represents $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ and $-\text{C}_3\text{H}_7$; and

X represents a chloride, bromide, iodide, fluoride, sulphate, bisulphate or nitrate ion.

15 2. An electrolyte as claimed in Claim 1 wherein the phthalocyanine radical brightening agent forms from 35 percent to 80 percent by weight of the total amount of the combination of brightening agents (a) and (b) present in the electrolyte.

3. An electrolyte as claimed in Claim 1 or 2 in which the combination of brightening agents (a) and (b) is present within a range of from 0.0005 to 1/g/l.

20 4. An electrolyte as claimed in Claim 1, 2 or 3 wherein the combination of brightening agents (a) and (b) is present in an amount of from 0.002 to 0.01 g/l.

5. An electrolyte as claimed in any one of Claims 1 to 4 including a supplemental brightening agent comprising a bath soluble and compatible polyether compound present in an amount of from 0.001 to 5 g/l.

25 6. An electrolyte as claimed in any one of Claims 1 to 5 including a supplemental brightening agent comprising a bath soluble and a compatible organic sulphide compound present in an amount of from 0.0005 to 1 g/l.

7. An electrolyte as claimed in any one of Claims 1 to 6, wherein the phthalocyanine radical brightening agent comprises Methic Turquoise.

30 8. An electrolyte as claimed in any one of Claims 1 to 6 wherein the apo safranine compound brightening agent comprises diethyl apo safranine.

9. An electrolyte as claimed in any one of Claims 1 to 6 wherein the phthalocyanine radical brightening agent comprises Methic Turquoise and the apo safranine compound brightening agent comprises diethyl apo safranine.

35 10. An electrolyte as claimed in any one of Claims 1 to 9 including halide ions in an amount up to 0.5 g/l.

11. A process for electrodepositing a bright, levelled copper deposit on a conductive substrate which comprises the steps of immersing a cathodically charged conductive substrate in an electrolyte as claimed in any one of Claims 1 to 10 and electrodepositing a copper plate on the substrate to the desired thickness.

12. A process as claimed in Claim 11 including controlling the temperature of the electrolyte within a range of from 15° to 50°C .

13. A process as claimed in Claim 11 or 12 including controlling the temperature of the electrolyte to within a range of about 20° to about 36°C .

45 14. A process as claimed in Claim 11, 12 or 13 including controlling the current density during the step of electrodepositing a copper plate on the substrate within a range of about 0.5 to about 400 ASF, (0.055 to 44 ASD).

15. A process as claimed in any one of Claims 11 to 14 including controlling the current density during the step of electrodepositing a copper plate on the substrate within a range of from 10 to 100 ASF (1.1 to 11 ASD).

16. A process as claimed in Claim 11 including controlling the temperature of the electrolyte within a range of from 20° to 36°C and controlling the average current density during the step of electrodepositing the copper plate on the substrate within a range of from 10 to 50 ASF (1.1 to 5.5 ASD).

55 17. An electrolyte substantially as herein described with reference to any one of the Examples.

18. A process for electrodepositing copper on a substrate substantially as herein described with reference to any one of the Examples.

60 19. A copper-plated substrate whose copper has been electrodeposited by means of an electrolyte as claimed in any one of Claims 1 to 10 and 17 and/or by a process as claimed in any one of Claims 11 to 16 and 18.